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A NEW INSTRUMENTAL TECHNIQUE FOR THE ANALYSIS OF HIGH ENERGY CONTENT FUELS

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This technical report has been reviewed and is approved for publication.

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The technical effort described herein was directed at determining the feasibility of using the Redox Chemiluminescence Detector (RCD) for the selective detection of cycloalkanes and antioxidants in jet fuels.

Three catalysts (gold, palladium, and platinum) were prepared and evaluated at several reaction temperatures. The gold catalyst at 300°C produced the best selectivity for cycloalkanes (40:1 for hexane and 3:1 for nonane). As temperature was increased, however, the selectivity for cycloalkanes decreased. The palladium and platinum catalysts did not demonstrate adequate selectivity under the examined test conditions.

Overall, the metal catalysts examined in this study did not exhibit sufficient selectivity to permit detection of cycloalkanes versus acyclic alkanes. The selectivity of the RCD for easily oxidized compounds (eg. phenols) versus hexane was typically 10^4 to 10^6.

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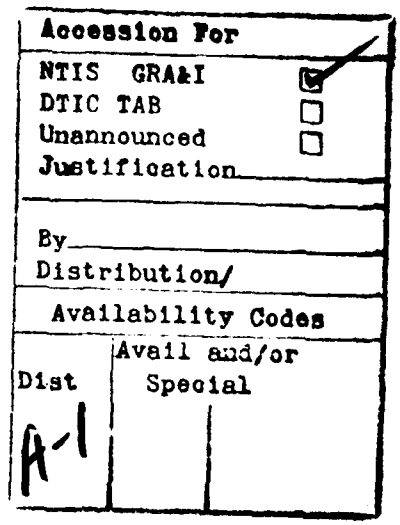
FOREWARD

This report describes the technical effort conducted under Air Force Contract No. F33615-86-2609, entitled "Analysis of High Density Fuels." All research conducted under this contract was administered under the direction of Mr. Paul C. Hayes, Jr., Project Engineer, Fuels Branch of the Aero propulsion and Power Laboratory, Wright Research and Development Center (WRDC) and Dr. Ric Hutte, Program Manager/ Principle Investigator, Sievers Research, Incorporated.



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INTRODUCTION

The purpose of this study is to determine the feasibility of using the Redox Chemiluminescence Detector (RCD) for the selective detection of cycloalkanes and antioxidants (e.g., 2,6-di-tert-butyl-4-methylphenol) in the presence of a complex matrix of noncyclic alkanes found in jet aircraft fuels. The RCD is a selective detector for gas chromatography (GC) based on two postcolumn reactions. In the first reaction, the effluent of the GC is mixed with a gas stream containing part per million levels of nitrogen dioxide (NO_2) and contacts a heated catalyst. At the catalyst surface, certain compound classes will rapidly react with NO_2 to form nitric oxide (NO) and oxidized species. The NO formed in this first reaction can be sensitively measured in a second chemiluminescent reaction in which NO reacts with ozone to form electronically excited NO_2, which subsequently emits a photon in the red and near-infrared region of the spectrum.

POST-COLUMN REACTION IN THE REDOX CHEMILUMINESCENCE DETECTOR

$$\text{Reducing agent} + NO_2 \xrightarrow{\text{Catalyst}} NO + \text{Oxidized species}$$

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$$

In the normal operation of the RCD, elemental gold is used as the catalyst at temperatures of 200 to 400 ^{o}C. Under these conditions, a wide range of compounds react with NO_2 including most oxygen-, nitrogen-, sulfur- and phosphorus-containing compounds, but saturated hydrocarbons and water do not appreciably react and are not detected. In contrast with gold, a more active metal such as palladium will promote reactions of saturated hydrocarbons with NO_2 to form NO.

In this study, we are investigating reaction conditions and metal catalysts which would result in the oxidation of cycloalkanes by NO_2 with formation of NO, without reaction of noncyclic hydrocarbons. This report summarizes our research results and possible future experiments.

EXPERIMENTAL

Instrumentation

The detector used in this study was a model 207 Redox Chemiluminescence Detector (Sievers Research, Inc.). The detector was connected to a Hewlett-Packard model 5890A gas chromatograph equipped with a split/splitless injection port, a

flame ionization detector and a 30 m x 0.32 mm ID cross-linked DB-5 (J&W Scientific) column with a 1 um film thickness. Helium carrier gas was used with a linear velocity of 30 cm/sec. Helium was also used to deliver the NO_2 reagent gas, by flowing 15 mL/min of He over a NO_2 permeation tube (VICI Metronics). The permeation tube NO_2 loss rate was 17 ug/min, resulting in an NO_2 concentration of ~600 ppm in the gas stream.

Catalysts

Three catalysts were prepared and evaluated for the selective detection of cycloalkanes versus noncyclic hydrocarbons. Gold-coated soda-lime glass beads were prepared by washing ~5 grams of 100 mesh glass beads (Potters Industry, Inc.) with methylene chloride and stirring with a solution of 1.3 grams of Engelhard Liquid Bright N-Au in 200 mL of methylene chloride. After evaporation of the solvent, the beads were heated slowly in air to 350 ^{o}C to remove the volatile constituents of the Liquid Bright residue and further heated to 650 ^{o}C. Palladium catalyst was prepared by evaporation of an aqueous solution of palladium chloride, followed by reduction under flowing hydrogen at 400 ^{o}C. The beads used for the palladium catalyst were 0.1 mm diameter borosilicate glass.

The platinum catalyst was Pt sponge (20 mesh) and was used as received from Alpha Products.

The catalyst beds were prepared by packing a 4 mm ID Pyrex glass tee with sufficient beads to form a bed approximately 1 cm in length. After installation, the catalysts were conditioned overnight at 500 °C under flowing NO_2/He.

Standard Samples

Five standard solutions were prepared for the determination of the selectivity and sensitivity of the RCD for cycloalkanes, normal alkanes, and other compounds which produce an RCD response. The compounds present in these samples, their concentrations and elution order are listed below:

J&W Polarity Test Mixture
(Solvent-methanol)

decane	0.11 mg/mL
1-octanol	0.07
2,6-dimethylphenol	0.20
2,6-dimethylaniline	0.04
naphthalene	0.18
1-decanol	0.10
tridecane	0.09
methyl decanoate	0.05
tetradecane	0.10

Nonane/Decaline Standard
(Solvent-Hexane)

n-nonane	7.2 mg/mL
trans-decalin	8.7

Normal Hydrocarbons Standard
(Solvent-hexane)

heptane	6.5 mg/mL
octane	3.4
nonane	6.0
decane	5.1
undecane	6.6
dodecane	6.6
tridecane	22.3
tetradecane	5.1
pentadecane	3.5

AF Standard
(Solvent-hexane)

nonane	0.53 mg/mL
1,2,3-trimethylcyclohexane	0.47
decane	0.51
trans-decalin	0.26
undecane	0.18
dodecane	0.18
naphthalene	1.68
tridecane	0.37
tetradecane	0.19
pentadecane	0.15
2,6-di-tert-butyl-4-methylphenol	0.60
9,10-dihydro-phenanthrene	0.17
1,2,3,4-tetrahydro-fluoranthene	0.35

RCD STANDARD
(Solvent-hexane)

1-heptanol	0.37 mg/mL
decane	0.76
2,6-dimethylphenol	0.63
naphthalene	1.48
tridecane	0.63
1-undecanol	0.34
tetradecane	0.53
2,6-di-tert-butyl-4-methyl phenol	0.53

RESULTS

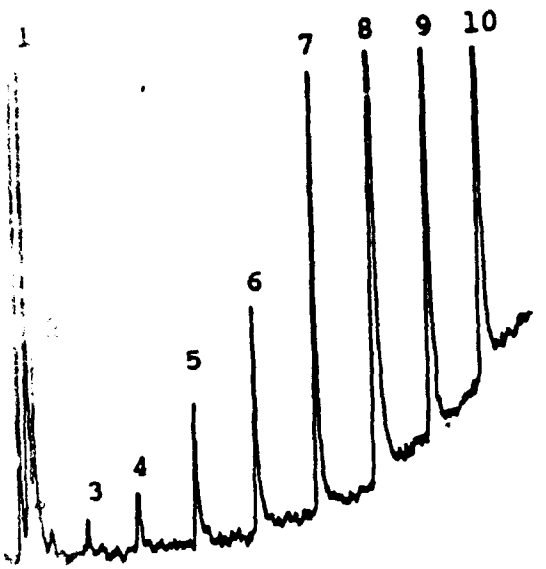
Gold Catalyst

As previously noted, saturated hydrocarbons generally do not rapidly react with NO_2 at a gold surface to form NO at the catalyst temperatures employed for the RCD (200 to 400 ^{o}C). However, when sufficiently large amounts of saturated hydrocarbons are injected, a small RCD response can be observed, even at catalyst temperatures as low as 300 ^{o}C, as shown in Figure 1. This sample also illustrates another characteristic of the gold catalyst currently used. The selectivity of the RCD for easily oxidized compounds (e.g., phenols) versus hexane is typically 10^4 to 10^6, but is less for the higher alkanes (i.e., higher alkanes produce a larger RCD response). One possible explanation based on kinetics is that the higher alkanes have longer residence times in the catalyst bed and react with NO_2, while the more volatile alkanes do not spend sufficient time on the gold surface to undergo appreciable reaction. An alternative explanation is that larger molecules can more readily undergo multi-stage reactions.

Based on this observation of high levels of saturated hydrocarbons producing a RCD response, some initial experiments were performed using a concentrated solution of n-nonane and trans-decalin in hexane. Typically, 2 uL injections were made using a split ratio of 35:1, corresponding to 400 ng of nonane, 500 ng of decalin and

RCD Conditions: Au Catalyst Temp. 300 °C, Integration Time 0.125 s
Integrator Conditions: Attenuation 2 ↑ 8, Chart Speed 0.5 cm/min

2 uL Normal Hydrocarbon Standard, Split Ratio 35:1



1.	Hexanes (Solvent)	3,800 ng
2.	Heptane	370
3.	Octane	194
4.	Nonane	340
5.	Decane	290
6.	Undecane	380
7.	Dodecane	380
8.	Tridecane	1,270
9.	Tetradecane	291
10.	Pentadecane	200

2 uL Nonane/Decaline Standard

1.	Hexanes (Solvent)	3,800 ng
2.	n-Nonane	410
3.	*trans*-decalin	500

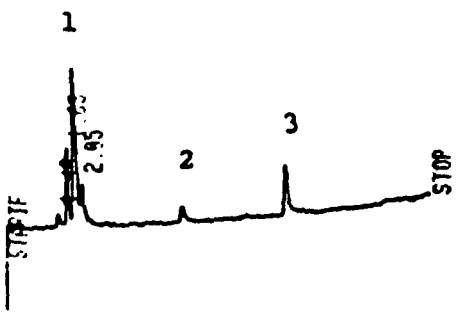


Figure 1. RCD RESPONSE FROM HIGH LEVELS OF NORMAL AND CYCLIC ALKANES WITH A GOLD CATALYST

38 ug of hexane on-column. The relative molar response factors (RMRF) were determined from the integrated areas of hexane, decalin and nonane as a function of gold catalyst temperature. In conjunction with these experiments, the RMRF for compounds known to be sensitively detected by the RCD were determined by analysis of the J&W polarity test mixture. The results from these experiments are shown in Tables 1 and 2.

Table 1. Relative Molar Response for trans-decalin versus hexane and nonane. (Average value from 5 Injections)

Au Catalyst Temperature	RMRF-C_6	RMRF-C_9
300 °C	39	3
350 °C	15	2
400 °C	14	2
Flame Ionization Detector	ND	1

D-Not Determined

Table 2. Relative Molar Response Ratios for Compounds that Produce a RCD Response

	Au Catalyst Temperature 300 °C	350 °C	400 °C	FID
n-decane	NR	NR	NR	0.6
1-octanol	1	1	1	1
2,6-dimethyl phenol	1.4	2.4	2.4	1.2
2,6-dimethyl aniline	1.5	2.5	3.2	1.4

Naphthalene	0.2	1.2	1.4	1.5
1-decanol	1.4	1.3	1.4	1.2
tridecane	NR	NR	0.1	2.1
methyl decanoate	0.7	1.5	1.4	1.6
tetradecane	NR	NR	0.1	2.2

NR-No RCD Response Observed

As shown in Table 1, at a relatively low gold catalyst temperature (300 ^{o}C) the molar response for trans-decalin is 40 times that of hexane, and three times that of n-nonane. As the temperature of the catalyst is increased, the absolute response from all compounds increases, but the selectivity for the cycloalkanes decreases. These response factors were obtained from injections of relatively large amounts of the normal and cyclic alkanes. When diluted samples containing decalin and nonane were injected (~50 ng on-column), no RCD response was observed for either compound, even at 400 ^{o}C.

To more closely simulate the amounts of cyclic and acyclic alkanes that would be found in a jet fuel, a standard was prepared containing C_9-C_{15} n-alkanes, 1,2,3-trimethylcyclohexane, trans-decalin, 2,6-ditert-butyl-4-methylphenol (BHT), naphthalene, and two partially hydrogenated aromatic hydrocarbons; 9,10-dihydro phenanthrene and 1,2,3,4-tetrahydro fluoranthene. A typical split injection (2 uL) of the standard gives 30 to 50 ng of the compounds on-column. At 400 ^{o}C, only decalin, naphthalene, C_{12}-C_{15} n-alkanes, BHT, and the two

partially hydrogenated PAH's produce RCD responses. However, at a gold catalyst temperature of 500 °C, all of the compounds can be detected and the relative molar response factors versus n-nonane at 500 °C and response factors obtained using a flame ionization detector are given in Table 3. At 500 °C, the gold catalyst shows little selectivity for the cyclic alkanes versus acyclic hydrocarbons.

Table 3. Relative Molar Response Factors
Au Catalyst Temperature 500 °C

	RCD	FID
Nonane	1	1
1,2,3-trimethylcyclohexane	1.1	1.0
Decane	1.4	1.1
trans-decaline	1.9	1.2
Undecane	1.4	1.3
Dodecane	1.6	1.4
Naphthalene	2.5	1.3
Tridecane	9.0	1.6
Tetradecane	13.3	1.6
Pentadecane	16.0	2.3
2,6-di-tert-butyl-4-methyl phenol	23.1	1.9
9,10-dihydro-phenanthrene	11.3	0.7
1,2,3,4-tetrahydro-fluoranthene	34.0	2.2

The results from these preliminary experiments indicate that the gold catalyst currently used with the RCD is not suitable for the selective detection of cyclic hydrocarbons in the presence of higher levels of acyclic alkanes. At low catalyst temperatures, some selectivity is observed, but only for high levels of the compounds. At higher catalyst temperatures, gold promotes the oxidation of both cyclic and acyclic alkanes. However, at

temperatures of 400 °C or lower, highly selectivity is observed for easily oxidizable compounds such as BHT, versus saturated hydrocarbons using a gold catalyst. Thus a gold catalyst is well suited for the analysis of these types of compounds in a hydrocarbon matrix such as jet fuel.

Pd Catalyst

Initial experiments have been performed using a palladium catalyst. As previously noted, Pd is a more active catalyst and promotes the reaction of NO_2 with low levels of saturated hydrocarbons at normal catalyst operating temperatures (200 to 400 °C). When the concentrated trans-decalin/n-nonane standard was injected into the GC using a Pd catalyst at 400 °C, hexane, trans-decalin, and nonane all produce a large RCD response. The relative molar response for decalin versus nonane using Pd at 400 °C was 3.1:1. A comparison of the selectivity of the Pd catalyst versus gold and a FID is shown in Table 4 and Figures 2 and 3.

After these initial experiments, additional tests were conducted to determine if higher selectivity for the cyclic hydrocarbons could be obtained at lower Pd catalyst temperatures. Two new catalyst beds were prepared from the same batch of Pd coated glass beads and conditioned overnight at 500 °C. Unlike the initial tests, these Pd catalyst beds showed substantially lower activity than the first Pd catalyst. Smaller RCD responses were observed

for all compounds, even at 500 °C and much lower responses were observed for the cyclic and acylic hydrocarbons. The relative molar response versus 1-heptanol for several compounds using these Pd catalysts and a Au catalyst are shown in Table 5.

TABLE 4. Relative Molar Response Ratios for Compounds that Produce a RCD Response with Pd and Au Catalyst

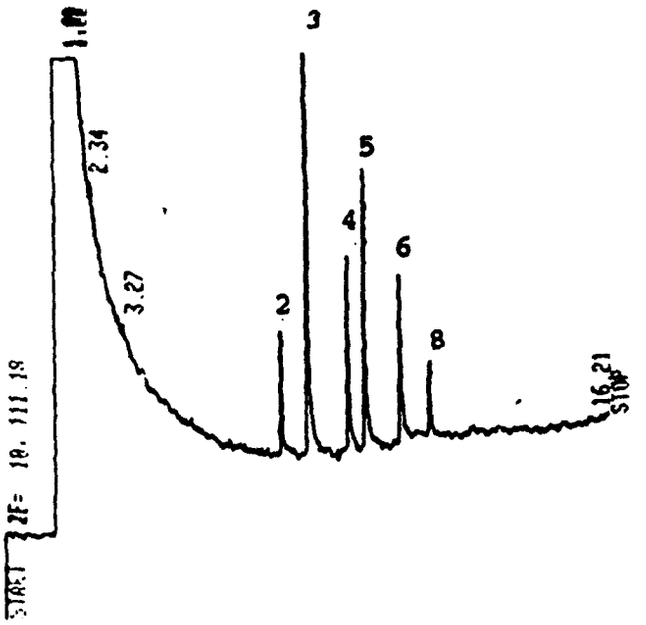
	Pd Catalyst 400 °C	Au Catalyst 400 °C	FID
n-decane	0.16	NR	0.6
1-octanol	1	1	1
2,6-dimethyl phenol	1.5	2.4	1.2
2,6-dimethyl aniline	2.0	3.2	1.4
naphthalene	0.7	1.4	1.5
1-decanol	1.2	1.4	1.2
tridecane	0.6	0.1	2.1
methyl decanoate	1.7	1.4	1.6
tetradecane	0.8	0.1	2.2

NR-No RCD Response Observed

In contrast to the earlier work using a Pd catalyst, the only compounds in the RCD test mixture to produce an RCD response at 400 °C were the alcohols, dimethylphenol and BHT. However, at 500 °C, these Pd catalysts did promote the reaction of hydrocarbons with NO_2 to form NO. The relative molar response ratios for normal alkanes, cyclic alkanes, BHT and the partially hydrogenated polycyclic aromatic hydrocarbons are shown in Table 6.

FIGURE 2. COMPARISON OF SELECTIVITY OF THE RCD WITH GOLD AND PALLADIUM CATALYSTS AND A FLAME IONIZATION DETECTOR

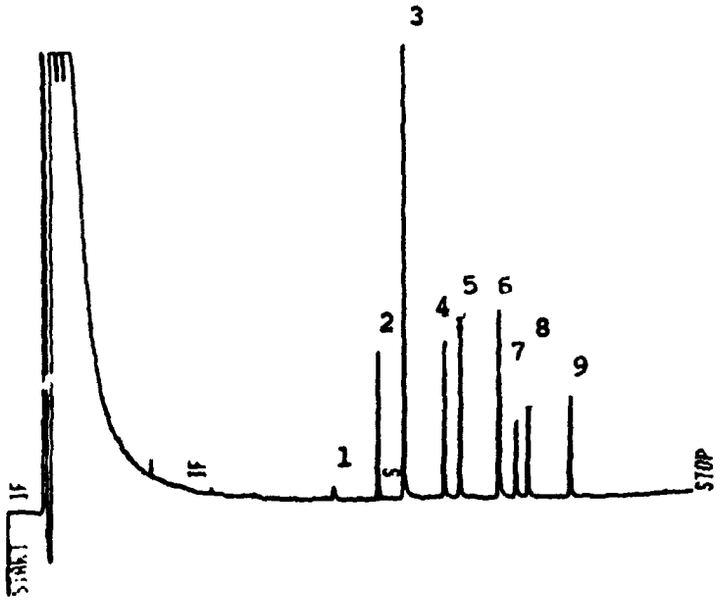
RCD Conditions: Au Catalyst Temp. 400 °C, Integration Time 0.125 s
Integrator Conditions: Attenuation 2 ↑ 8, Chart Speed 0.5 cm/min



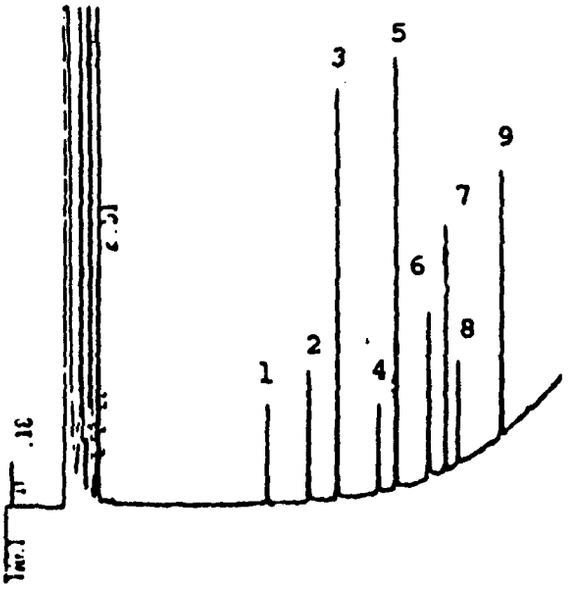
2 uL J&W Polarity Test Mixture
(Solvent-Methanol)

1.	Decane	6 ng
2.	1-Octanol	4
3.	2,6-dimethylphenol	11
4.	2,6-dimethylaniline	2
5.	Naphthalene	10
6.	1-Decanol	6
7.	Tridecane	5
8.	Methyl decanoate	3
9.	Tetradecane	6

RCD Conditions: Pd Catalyst Temp. 400 °C,
Integration Time 0.003 s
Integrator Conditions: Attenuation 2 ↑ 8,
Chart Speed 0.5 cm/min



FID Conditions: Detector Temp. 300 °C,
Range 4 Attn 2 ↑ 4



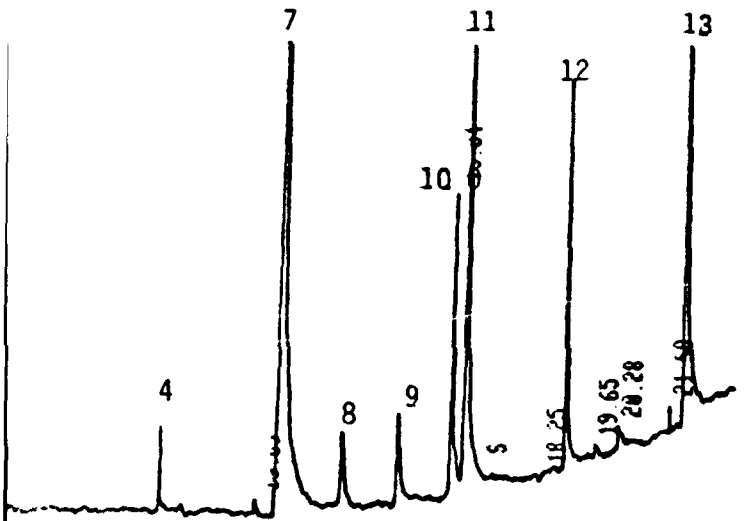
(Note: Chromatogram from first Pd catalyst tested)

FIGURE 3. COMPARISON OF SELECTIVITY OF RCD USING GOLD AND PALLADIUM CATALYSTS AND FID FOR HYDROCARBONS

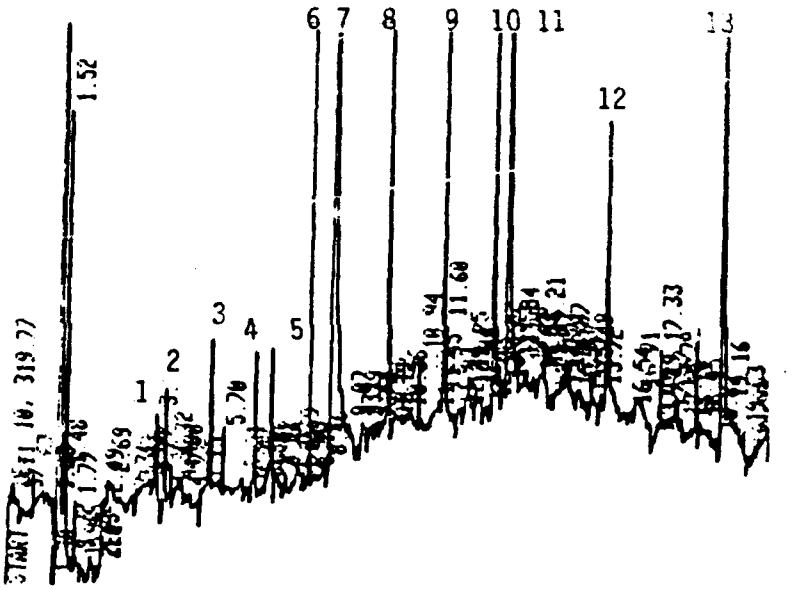
4 uL AF Standard
(Solvent-Hexane)

1.	Nonane	61 ng
2.	1,2,3-trimethylcyclohexane	54
3.	Decane	58
4.	*trans*-decalin	30
5.	Undecane	21
6.	Dodecane	21
7.	Naphthalene	192
8.	Tridecane	42
9.	Tetradecane	22
10.	Pentadecane	17
11.	2,6-di-*tert*-butyl-4-methylphenol	69
12.	9,10-dihydro-phenanthrene	19
13.	1,2,3,4-tetrahydro-fluoranthene	40

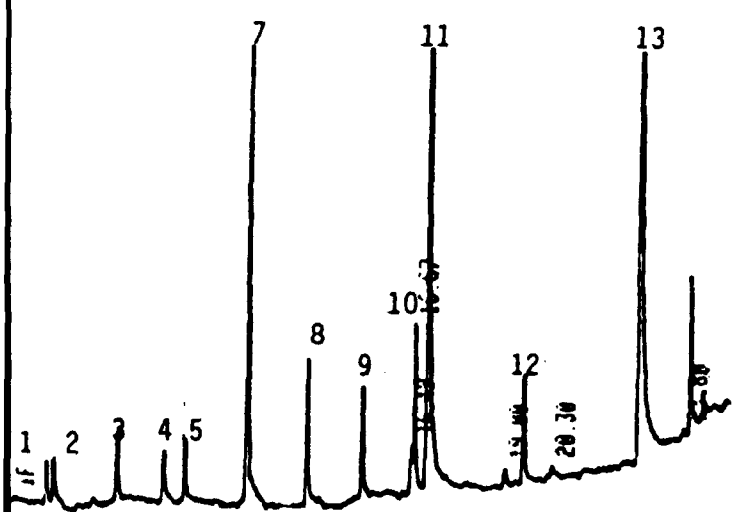
Au Catalyst Temp. 400 °C



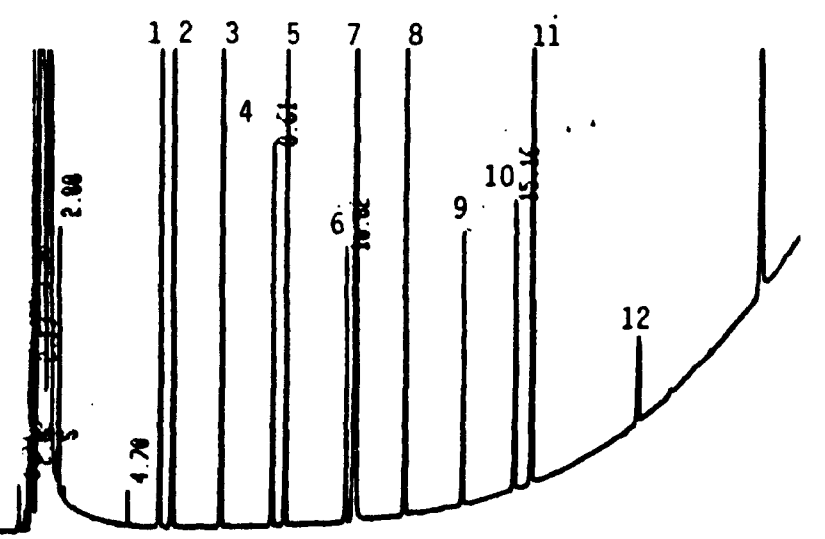
Au Catalyst Temp. 500 °C



Pd Catalyst Temp. 500 °C



FID



(Note: Chromatogram from second, less sensitive Pd catalyst tested)

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Table 5. Relative Molar Response Ratios for Compounds that Produce a RCD Response with Pd and Au Catalyst

	Pd Catalyst 500 °C	Au Catalyst 400 °C
n-decane	0.04	NR
1-heptanol	1	1
2,6-dimethyl phenol	1.1	2.7
naphthalene	0.06	0.4
tridecane	0.1	NR
1-undecanol	1.7	1.7
tetradecane	0.1	NR
2,6-di-tert-butyl-4-methyl phenol	2.1	1.9

NR-No RCD Response Observed

Table 6. Relative Molar Response Factors Pd Catalyst Temperature 500 °C

Nonane	1
1,2,3-trimethylcyclohexane	1.8
Decane	1.8
trans-decaline	2.9
Undecane	2.0
Dodecane	2.7
Naphthalene	4.8
Tridecane	5.5
Tetradecane	8.4
Pentadecane	19.4
2,6-di-tert-butyl-4-methyl phenol	69.8
9,10-dihydro-phenanthrene	11.1
1,2,3,4-tetrahydro-fluoranthene	110.2

At present, we have no explanation for the different reactivities observed for the different Pd catalysts. Based on the results obtained using the less active Pd catalyst, apparently suitable reaction conditions for the selective detection of cycloalkanes versus acyclic alkanes cannot be achieved using palladium.

Pt Catalyst

The last metal catalyst tested for the selective detection of cycloalkanes was platinum. In contrast to the Au and Pd, the Pt catalyst used was the pure metal sponge without a glass bead support. The catalysts bed was prepared by packing the sponge into the glass tee in the same manner used for the Au and Pd beds. The catalyst was conditioned overnight at 500 ^{o}C in a flowing NO_2/He stream. The catalyst temperature was lowered to 400 ^{o}C and the selectivity and sensitivity was determined by the analysis of the standard test mixtures.

Even after the catalyst temperature had stabilized, a high NO background was observed using the Pt catalyst. The amount of NO formed from decomposition of NO_2 on the Pt surface at 400 ^{o}C is approximately 10 times the amount observed using a gold catalyst at the same temperature. The Pt catalyst was also not as active in promoting the reactions of analytes with NO_2 as either Au or Pd. No RCD response was observed for saturated hydrocarbons (cyclic or acyclic) even when microgram quantities were injected. Analysis of the RCD test mixture showed only the alcohols,

dimethylphenol and BHT react to form NO. The relative molar response ratios for these compounds are given in Table 7 and a comparison of the selectivity of gold, palladium and platinum catalysts is shown in Figure 4.

Table 7. Relative Molar Response Factors
Pt Catalyst Temperature 400 °C

n-decane	NR
1-heptanol	1
2,6-dimethyl phenol	2.2
naphthalene	NR
tridecane	NR
1-undecanol	3.2
tetradecane	NR
2,6-di-tert-butyl-4-methyl phenol	1.1

NR-No RCD Response Observed

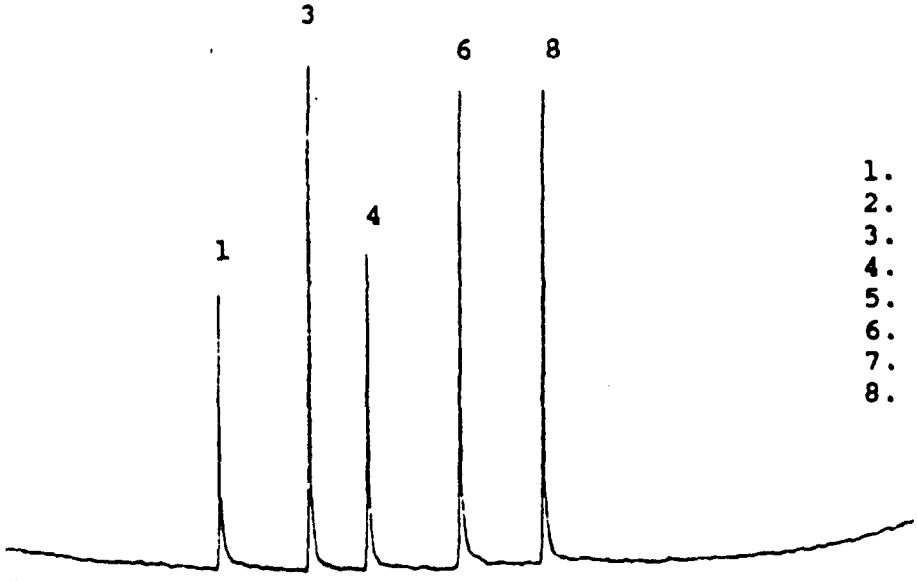
At temperature above 400 °C, the background NO from thermal decomposition was too large to permit operation of the RCD even on the shortest (least sensitive) integration time. Thus Pt is not a suitable catalyst for use with the RCD.

Authentic Samples

Two samples of jet fuel were analyzed by RCD with the Au catalyst as part of this study. The first sample was a Navy JP-5 which

FIGURE 4. COMPARISON OF SELECTIVITY OF RCD USING GOLD, PALLADIUM AND PLATINUM CATALYSTS

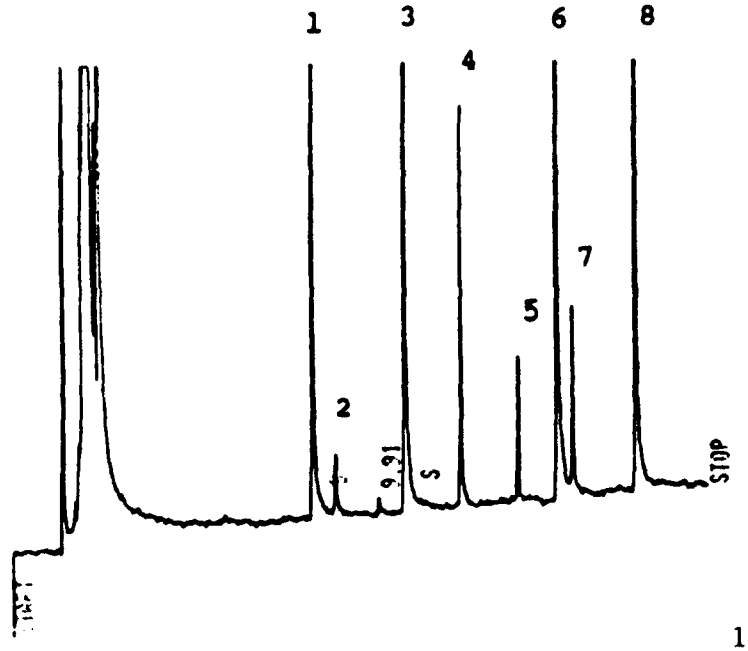
RCD Conditions: Au Catalyst Temp. 400 °C, Integration Time 0.25 s
Integrator Conditions: Attenuation 2 ↑ 8, Chart Speed 0.5 cm/min



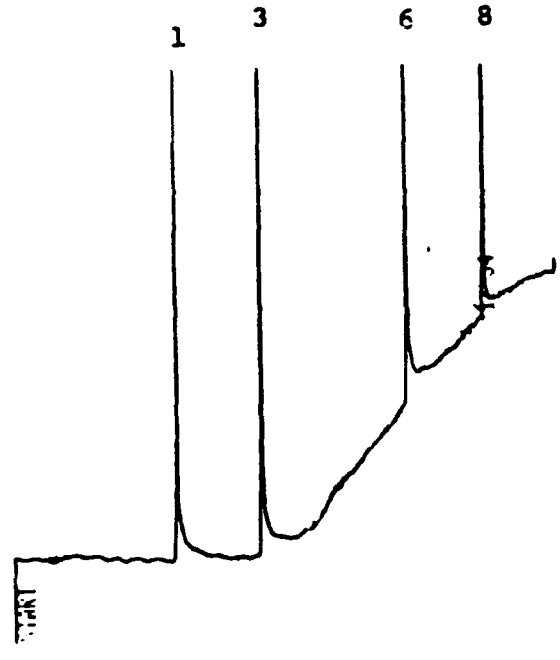
2 uL RCD STANDARD
(Solvent-hexane)

1. 1-heptanol	21ng
2. decane	43
3. 2,6-dimethylphenol	36
4. naphthalene	85
5. tridecane	36
6. 1-undecanol	19
7. tetradecane	30
8. 2,6-di-*tert*-butyl-4-methyl phenol	30

RCD Conditions: Pd Catalyst Temp. 500 °C,
Integration Time 0.125 s
(Note: Chromatogram from second, less sensitive Pd catalyst tested)



RCD Conditions: Pt Catalyst Temp. 400 °C,
Integration Time 0.01 s



contains 24 ppm of an anti-oxidant A029, which is principally 2,6-di-tert-butyl-4-methyl phenol (BHT), received from the Naval Research Laboratory. Figure 5 shows the chromatograms obtained at three different gold catalyst temperatures. At 300 ^{o}C, only two major components are observed, BHT and an unidentified component. As the catalyst temperature is increased, some of the components of the fuel, possibly aromatic hydrocarbons or olefins are also detected, but BHT and the unknown component are still the most sensitively detected compounds in the sample.

The second sample analyzed was a jet fuel containing high levels of cycloparaffins (85-POSF-2265 JP-8X) received from the Air Force. This sample was analyzed using the RCD with a gold catalyst at 400 ^{o}C and using flame ionization detection and the FID and RCD chromatograms are shown in Figure 6. On the basis of retention times, normal alkanes were identified in the FID chromatogram, but the two cycloalkanes on hand (decalin and trimethylcyclohexane) were not detected in this sample. Far fewer compounds were observed using RCD and based on retention times, the normal alkanes were not detected by the RCD in this sample.

Future Studies

While the metal catalysts tested in this study do not exhibit sufficient selectivity to permit detection of cycloalkanes versus acyclic alkanes by the principal of redox chemiluminescence,

FIGURE 5. RCD ANALYSIS OF ANTI-OXIDANT IN NAVY JET FUEL

RCD Conditions: Au Catalyst Temp. 300-400 °C, Integration Time 0.25 s
Integrator Conditions: Attenuation 2 ↑ 8, Chart Speed 0.5 cm/min
Sample: ~0.8 uL JP-5 (neat) containing 24 ppm AO29 (BHT), split 35:1

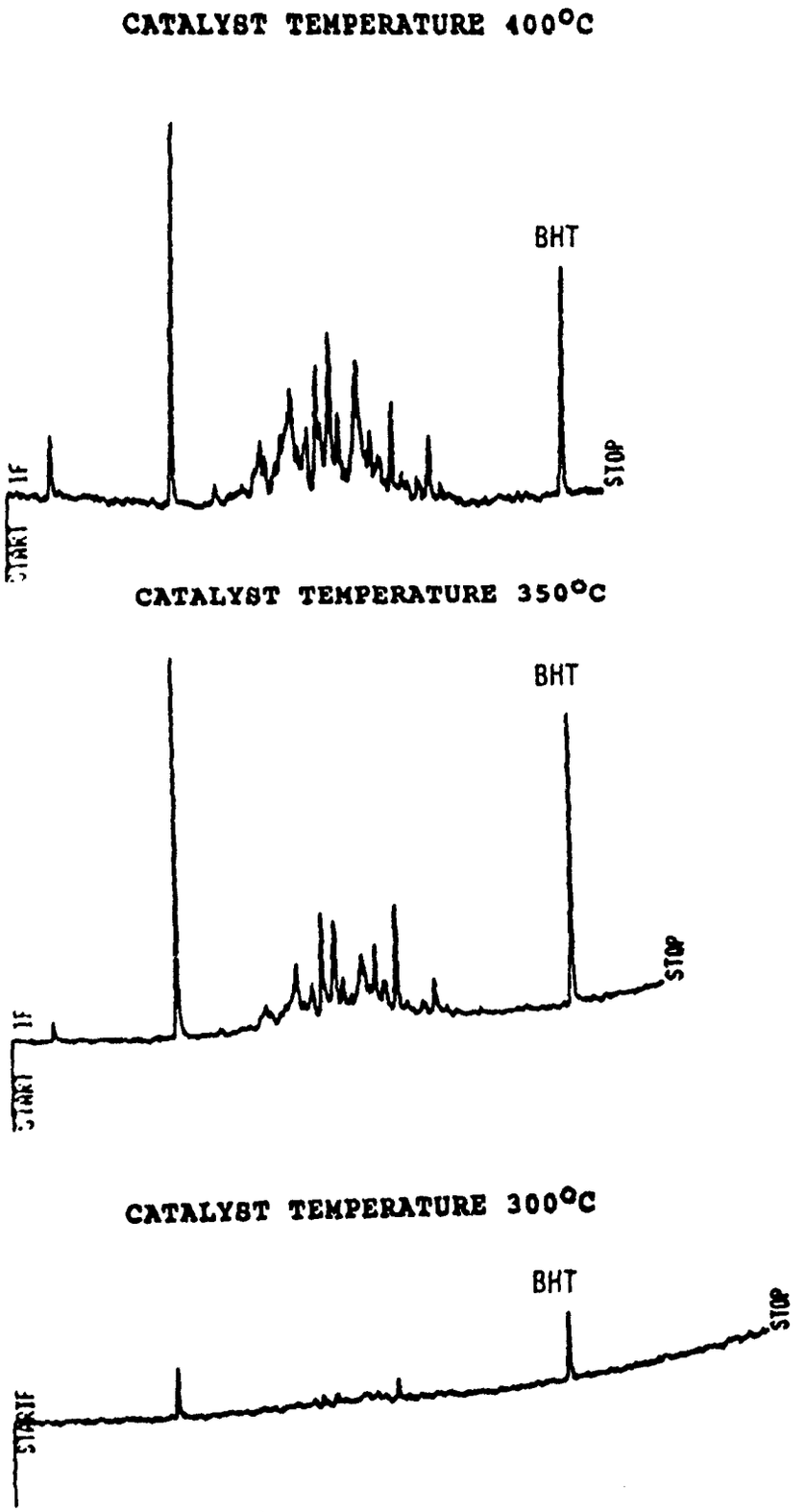
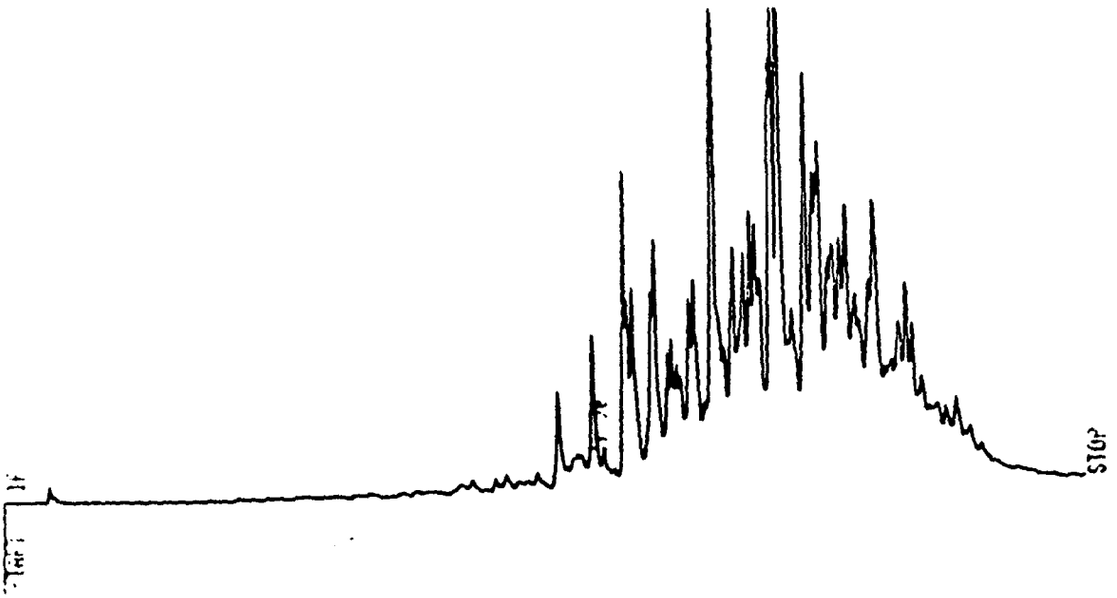


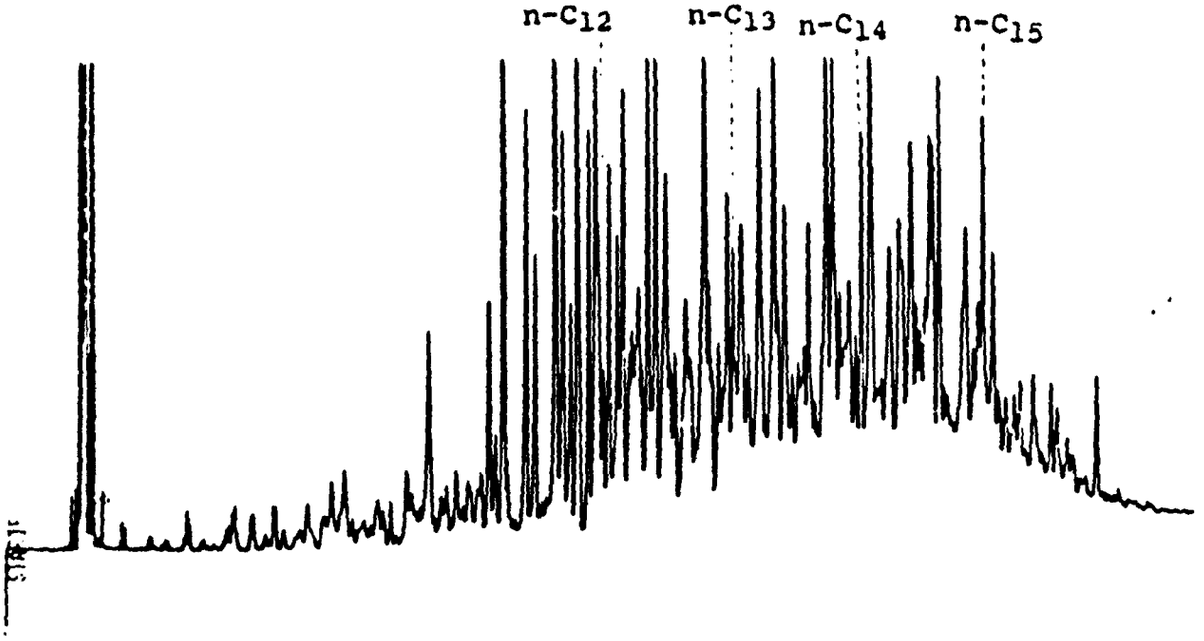
FIGURE 6. ANALYSIS OF HIGH DENSITY AIR FORCE JP-8 JET FUEL

RCD Conditions: Au Catalyst Temp. 400 °C, Integration Time 0.125 s
Integrator Conditions: Attenuation 2 ↑ 8, Chart Speed 0.5 cm/min

Sample: ~0.2 uL JP-8 (neat), split 35:1



FID Conditions: Detector Temp. 300 °C, Range 4 Attn 2 | 4
Integrator Conditions: Attenuation 2 ↑ 4, Chart Speed 0.5 cm/min



several additional metals and catalysts deserve further study. Metals such as rhodium, ruthenium, and other transition metals may exhibit selective oxidation of the cycloparaffins. Metal alloys may also prove useful, particularly combining an active metal (e.g., Pd) with a less active one (e.g., Au or Pt). At present it is not known what activity such alloys would exhibit.

A second factor that may be important in determining the activity of the catalyst is the nature of the support. Catalysts using more traditional supports such as silica or alumina may exhibit different selectivities.

Finally, other materials may catalyze the selective oxidation of cycloparaffins. One attractive candidate is molecular sieves (zeolites). Some initial studies indicate the 13X molecular sieves can be used as catalysts in the RCD, even in the absence of gold or palladium. Proper choice of zeolite may permit selective detection by combining metal-catalyzed oxidation with some form of size exclusion of other discrimination based on the shapes of the compounds. These possibilities for selective detection of cycloalkanes and the development of a GC method for the analysis of the "dimer acid" corrosion inhibitor used in Air Force jet fuels will be the subject of a future proposal.

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